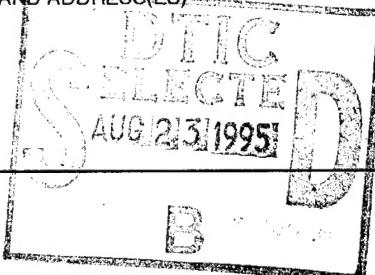


## REPORT DOCUMENTATION PAGE

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1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE 15 August 1995	3. REPORT TYPE AND DATES COVERED 6/94 - 5/95	5. FUNDING NUMBERS N00014-91-J-1909 R&T Code 4133035 Robert J. Nowak
4. TITLE AND SUBTITLE Evidence for Specific and Non-Specific Adsorption of ClO <sub>4</sub> on Ag(110)		6. AUTHOR(S) A. Krasnopoler and E. M. Stuve	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Washington Department of Chemical Engineering Box 351750 Seattle, WA 98195-1750		8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report No. 4	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Street Arlington, VA 22217		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES 			
12a. DISTRIBUTION / AVAILABILITY STATEMENT This document has been approved for public release and sale; its distribution is unlimited.		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The coadsorption of ClO <sub>4</sub> with H <sub>2</sub> O on Ag(110) was studied as a model of anion adsorption at the solid-liquid interface. Thermal desorption spectroscopy, low energy electron diffraction, and high resolution electron energy loss spectroscopy were used to investigate the interactions between perchlorate, water and the metal surface. The vibrational spectrum of adsorbed ClO <sub>4</sub> is an indicator of its adsorption geometry. For ClO <sub>4</sub> adsorbed on the clean surface, losses at 640, 915, 1020 and 1220 cm <sup>-1</sup> indicate that adsorption occurs through three oxygen atoms (tridentate) with a symmetry of C <sub>3v</sub> or lower. When coadsorbed with H <sub>2</sub> O, the vibrational spectrum resembles that of fully solvated, tetrahedral ClO <sub>4</sub> <sup>-</sup> (T <sub>d</sub> symmetry) with bands at 610, 880 and 1090 cm <sup>-1</sup> . The increase in symmetry indicates that direct interaction with the metal is lost and is considered evidence for non-specifically adsorbed ClO <sub>4</sub> in UHV. The thermodynamic feasibility of this process is also discussed.			
14. SUBJECT TERMS Double Layer Modeling, Nonspecific Adsorption, Perchlorate Ion, Silver(110), Metal/Electrolyte Interface		15. NUMBER OF PAGES 19	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT

**OFFICE OF NAVAL RESEARCH**

Research Contract N00014-91-J-1909

R&T Code 4133035

Program Manager Robert J. Nowak

Technical Report No. 4

"Evidence for Specific and Non-Specific Adsorption of ClO<sub>4</sub> on Ag(110)"

by

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Prepared for Publication

in

Journal of Vacuum Science & Technology A, 13 (1995) 1681-1686

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August, 1995

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# EVIDENCE OF SPECIFIC AND NON-SPECIFIC ADSORPTION OF PERCHLORATE ( $\text{ClO}_4$ ) ON SILVER(110)

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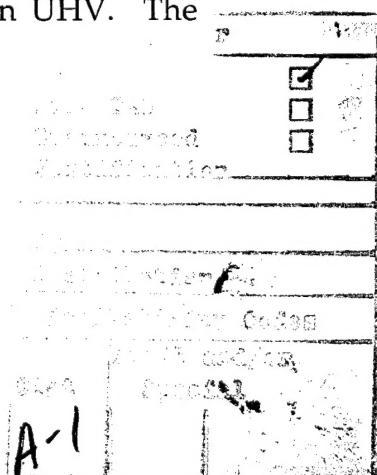
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Submitted to the *Journal of Vacuum Science and Technology A*, September, 1994

Revised, February, 1995

## Abstract

The coadsorption of  $\text{ClO}_4$  with  $\text{H}_2\text{O}$  on  $\text{Ag}(110)$  was studied as a model of anion adsorption at the solid-liquid interface. Thermal desorption spectroscopy, low energy electron diffraction, and high resolution electron energy loss spectroscopy were used to investigate the interactions between perchlorate, water and the metal surface. The vibrational spectrum of adsorbed  $\text{ClO}_4$  is an indicator of its adsorption geometry. For  $\text{ClO}_4$  adsorbed on the clean surface, losses at 640, 915, 1020 and  $1220\text{ cm}^{-1}$  indicate that adsorption occurs through three oxygen atoms (tridentate) with a symmetry of  $\text{C}_{3v}$  or lower. When coadsorbed with  $\text{H}_2\text{O}$ , the vibrational spectrum resembles that of fully solvated, tetrahedral  $\text{ClO}_4^-$  ( $\text{T}_d$  symmetry) with bands at 610, 880 and  $1090\text{ cm}^{-1}$ . The increase in symmetry indicates that direct interaction with the metal is lost and is considered evidence for non-specifically adsorbed  $\text{ClO}_4$  in UHV. The thermodynamic feasibility of this process is also discussed.



## I. INTRODUCTION

Models of the electrochemical interface have been investigated in UHV by various surface-sensitive techniques in order to probe the molecular level interactions between the metal and the electrolyte.<sup>1-8</sup> They often involve anions directly adsorbed to the metal (so-called specific adsorption) prior to the addition of solvent. To model non-specific adsorption requires the formation of a stable ion in the adsorbed layer that is not in contact with the surface. The only known example of a non-specifically adsorbed species in UHV is the formation of hydronium from coadsorbed H and H<sub>2</sub>O on the (111) and (100) surfaces of platinum.<sup>7,8</sup> The perchlorate ion is one of the most likely candidates to model the anionic counterpart of this behavior by virtue of its tendency for non-specific adsorption electrochemically and because it can be generated in UHV. Coadsorption of water and perchlorate thus offers the opportunity for direct evidence of non-specific adsorption of an anion in UHV.

Because perchlorate is polyatomic, changes in its internal vibrational modes will reflect changes in its adsorption environment. In potential-dependent infra-red (IR) studies of Pt(111) in perchloric acid solution, a band at 1200-1234 cm<sup>-1</sup> appears between 575 and 1100 mV NHE (normal hydrogen electrode) in addition to that of the ion in solution at 1100-1119 cm<sup>-1</sup>.<sup>9</sup> The change from low to high vibrational frequency band represents the change from hydrated, solution phase ClO<sub>4</sub><sup>-</sup> to specifically adsorbed ClO<sub>4</sub>.

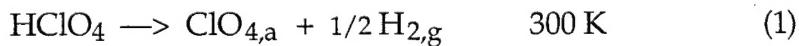
With the bonding of ClO<sub>4</sub> to the metal, the tetrahedral symmetry of the perchlorate ion is lowered to an extent that depends on the number of bonds formed with the metal, which varies from one (monodentate) to two (bidentate) to three (tridentate). For monodentate or tridentate coordination, the T<sub>d</sub> symmetry of ClO<sub>4</sub><sup>-</sup> would be lowered to C<sub>3v</sub> if the symmetry of the substrate is ignored, while for bidentate coordination, the symmetry would be lowered further to C<sub>2v</sub>. Although coordination of a perchlorate

molecule to a metal surface is expected to differ from coordination to a single metal atom, spectra of perchlorate salts of the latter can serve as standards for the vibrations of  $\text{ClO}_4$  as a function of symmetry and coordination. The modes observed by IR spectroscopy for  $\text{Cu}(\text{ClO}_4)_2$  and  $\text{Cu}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ <sup>10</sup> and by Raman and IR spectroscopy of rare-earth metal perchlorates<sup>11</sup> are shown in Table I, along with those observed for the perchlorate ion in solution.<sup>12</sup> As the symmetry is lowered, the degeneracy of the asymmetric Cl-O stretch is removed and additional vibrational modes appear in the spectrum. The number of observed vibrational modes can then be used to evaluate the symmetry of adsorbed perchlorate and how it is affected by coadsorbed water.

## II. EXPERIMENTAL PROCEDURE

The experiments were conducted in stainless steel UHV chamber that has been described previously.<sup>4,6,8</sup> The typical resolution (full width at half-maximum, FWHM) of the high resolution electron energy loss spectrometer (HREELS) was  $100 \text{ cm}^{-1}$ , and all energy losses are rounded to the nearest  $5 \text{ cm}^{-1}$ . EELS spectra were collected at a sample temperature of 110 K following adsorption or annealing.

Adsorbed perchlorate was produced by heating perchloric acid, adsorbed at 110 K, to 300 K to remove hydrogen, excess perchloric acid and any coadsorbed water from the surface, as shown in eqn. (1). Estimates of coverage are based on the observed LEED patterns and comparison to previous results.<sup>13</sup>



Water and  $\text{HClO}_4$  vapor were introduced sequentially through a common glass capillary array doser.<sup>14</sup> Dosing was conducted with the array positioned within 2 mm of the sample.  $\text{H}_2\text{O}$  coverages were calculated from integration of the mass spectrometer signal during thermal desorption and calibration using known

standards.<sup>4,15</sup> They are reported in terms of monolayers (ML) of the topmost Ag atoms of the perfect (110) surface:  $8.45 \times 10^{14} \text{ cm}^{-2}$ .

An approximate measure of work function change was taken from the change in sample bias potential in HREELS required to maximize the intensity of the elastic peak. This method works so long as the region in the vicinity of the sample is free of electric fields. This condition was satisfied by tuning the spectrometer such that a spectrum of the clean surface was obtained without an applied radial deflection of the electron beam as it exited the monochromator or entered the analyzer. Radial deflection of the electron beam changes the direction of the electron beam along a direction normal to the surface. Shifts in work function due to adsorption introduce electric fields around the sample, which deflect the electron beam and degrade the measured spectrum, unless the change in work function is compensated, and a field-free region restored, by changing the sample bias. The reference bias for the clean Ag(110) surface was 0.0 V with respect to ground. A positive sample bias therefore represents an increase in work function and a negative sample bias a decrease in work function with respect to the clean surface.

### III. RESULTS

#### A. Adsorbed ClO<sub>4</sub>

Fig. 1 shows EEL spectra for adsorbed perchlorate at 110 K. The observed LEED patterns associated with the surface examined in spectra (a) and (c) were (1x1) and c(2x2), respectively. This corresponds to coverages of < 0.2 ML and 0.5 ML, according to previous data.<sup>13</sup> Peaks below 1600 cm<sup>-1</sup> are due to fundamental modes of perchlorate. Strong peaks are observed at 640, 915 and 1220 cm<sup>-1</sup> and a weak band is observed at 1020 cm<sup>-1</sup>. The bias potential was increased from 0.0 V (clean surface) to 1.9 V in spectrum (a), indicating an increase in work function due to adsorbed perchlorate. In spectrum (c), the radial deflection of the beam entering the analyzer was nonzero, so

the change in sample bias could not be used to measure work function.

Above 1600 cm<sup>-1</sup>, the peaks at 2990 and 3555 cm<sup>-1</sup> are assigned to O-H stretches of water interacting with perchlorate. The adsorbed water came from the background gas in the UHV chamber and amounted to just 0.04 ML as judged from the thermal desorption peak at 200 K in fig. 2(a). When the ClO<sub>4</sub> coverage was increased to 0.5 ML, desorption of 0.06 ML H<sub>2</sub>O, again adsorbed from residual H<sub>2</sub>O, occurred at a higher temperature of 220 K, as shown in fig. 2(c). The peak at 2350 cm<sup>-1</sup> in fig. 1(a) is most likely an overtone of the peak at 1220 cm<sup>-1</sup>, as it exhibits the same width as the other perchlorate peaks, while the O-H stretching peaks are slightly broader.

## B. Coadsorption of ClO<sub>4</sub> and H<sub>2</sub>O

Following the thermal desorption curve of fig. 2(a), water was adsorbed at 100 K and the sample heated to 170 K to ensure desorption of any multilayers. For the EELS measurement the sample bias was reduced to 0.1 V, indicating that the work function was close to that of the clean surface. The resulting spectrum, shown in fig. 1(b), is markedly different from that for adsorbed ClO<sub>4</sub> alone. The peak at 200 cm<sup>-1</sup> is assigned to frustrated translation of H<sub>2</sub>O. The 725 cm<sup>-1</sup> peak is assigned to H<sub>2</sub>O libration, but shoulders of this peak at 610 and 880 cm<sup>-1</sup> are due to contributions from ClO<sub>4</sub> or a combination mode of the frustrated translation and libration. The sharp peaks at 915 and 1220 cm<sup>-1</sup> seen in (a) have been replaced by a broader feature at 1090 cm<sup>-1</sup>. A distinct H<sub>2</sub>O scissoring mode appears at 1635 cm<sup>-1</sup>. A broad band at 3545 cm<sup>-1</sup> dominates the O-H stretching region with a smaller peak at 3000 cm<sup>-1</sup>. The H<sub>2</sub>O thermal desorption in fig. 2(b), measured after the EELS spectrum, shows a single peak at 190 K and an area corresponding to a coverage of 0.62 ML. This places the ratio of H<sub>2</sub>O to ClO<sub>4</sub> at greater than three, given the initial perchlorate coverage of less than 0.2 ML mentioned above, and is consistent with previously measured H<sub>2</sub>O/ClO<sub>4</sub> ratios.<sup>13</sup>

For 0.5 ML of perchlorate,  $\text{H}_2\text{O}$  was again adsorbed to 0.33 ML at 100 K and the EEL spectrum measured as shown in fig 1(d). In contrast to the results for the lower perchlorate coverage (b), the peaks due to adsorbed  $\text{ClO}_4$  at 640, 915 and  $1240\text{ cm}^{-1}$  observed for the nominally water-free surface (c) are not removed by coadsorption of  $\text{H}_2\text{O}$ , but the intensities of these three peaks have decreased. Although a librational peak near  $725\text{ cm}^{-1}$  is absent in (d) evidence of adsorbed water is seen in the development of the internal  $\text{H}_2\text{O}$  bending and stretching modes, respectively, at approximately  $1630\text{ cm}^{-1}$  and in a region extending from  $2700$  to  $3700\text{ cm}^{-1}$  with a peak at  $3540\text{ cm}^{-1}$ . Subsequent thermal desorption in fig. 2(d) shows a smaller  $\text{H}_2\text{O}$  desorption peak at 190 K, in comparison to fig. 2(b), and the appearance of a shoulder at 210 K.

#### IV. DISCUSSION

##### A. Bonding of $\text{ClO}_4$ to $\text{Ag}(110)$

The electron energy losses of fig. 1 are compared to those of metal perchlorate complexes and ionic perchlorate in Table I. In terms of the number of identifiable bands, the spectrum for the adsorbed perchlorate (without water) compares favorably with those of  $\text{Cu}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{M}(\text{ClO}_4)_3$  where M is a rare-earth metal, indicating  $\text{C}_{3v}$  symmetry. Good agreement is found between the peak at  $1220\text{ cm}^{-1}$  observed for  $\text{ClO}_4/\text{Ag}(110)$  and the Cl-O stretch in the tridentate  $\text{M}(\text{ClO}_4)_3$ . Conversely, the  $915\text{ cm}^{-1}$  peak agrees better with the Cl-O stretch of the monodentate species. This disagreement suggests that a definitive assignment of the adsorption of perchlorate cannot be made based on the vibrational spectrum alone. For this, additional structural information, such as that provided by LEED and electron stimulated desorption ion angular distribution (ESDIAD), is required.

For 0.1 ML  $\text{ClO}_4$ , the appearance of two  $\text{O}^+$  ESDIAD lobes along the [001] direction were assigned to a bidentate perchlorate adsorbed atop a single Ag atom in the

trough.<sup>13</sup> At 0.5 ML ClO<sub>4</sub>, the O<sup>+</sup> emission changes to two lobes along the [110] direction, and a bidentate structure rotated 90° from the first was proposed. However, these models are contradicted by the energy loss data which favor either the monodentate or tridentate forms. Fig. 3(a) shows a model that rectifies the differing interpretations of the ESDIAD and HREELS data. For 0.1 ML ClO<sub>4</sub> one oxygen atom resides in a (111) site of the trough while the other two reside on ridge atoms. The terminal Cl-O bond is tilted away from the surface normal and toward the [001] direction to give agreement with the ESDIAD data. Fig. 3(b) shows the change in perchlorate adsorption when the ClO<sub>4</sub> coverage is increased to 0.5 ML. The perchlorate molecules are adsorbed in a c(2x2) structure (as indicated by LEED), but rotated 90° from its orientation in fig. (a), such that the terminal Cl-O bond is tilted along the [110] direction, as prescribed by the observed O<sup>+</sup> ESDIAD emission.<sup>13</sup>

The models of fig. 3 are intended to illustrate the coordination of perchlorate to the surface (e.g., tridentate vs. bidentate or monodentate) and the tilting of the outwardly pointing Cl-O bond from the surface normal. The exact surface bonding sites of perchlorate are as yet unknown, but the models of fig. 3 indicate the bonding sites expected on the basis of maximum coordination of the oxygen atoms contacting the surface with the surface atoms themselves. Tridentate coordination is chosen over monodentate because of the greater availability of coordination sites on the metal surface as compared to a single metal atom. Monodentate adsorption would also not concur with the ESDIAD results. If the perchlorate were adsorbed normal to the surface, the O<sup>+</sup> emission would appear as a halo if the molecule were rotating, as is observed for NH<sub>3</sub> on Ru(001),<sup>16</sup> or as six lobes if it were rigid due to the three oxygen atoms and the two-fold symmetry of the (110) surface. The only other way to conform to the ESDIAD data would be to have the Cl-O bond to the metal tilted such that only one Cl-O bond was directed away from the surface. This would require the other two

oxygen atoms to approach the surface, making the adsorption effectively tridentate. The case for bidentate adsorption is effectively ruled out on the basis of the energy loss results.

### B. $\text{ClO}_4/\text{Ag}(110)$ : Model Specific Adsorption

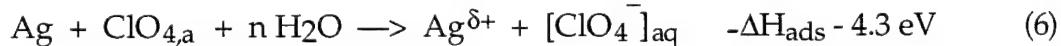
The  $1220\text{ cm}^{-1}$  loss observed for  $\text{ClO}_4/\text{Ag}(110)$  is in excellent agreement with the previously measured, in-situ IR absorption at  $1218\text{-}1234\text{ cm}^{-1}$  for  $\text{Pt}(111)$  in perchloric acid electrolyte.<sup>9</sup> In accord with that study, the  $1220\text{ cm}^{-1}$  band is assigned to the asymmetric Cl-O stretch of specifically adsorbed  $\text{ClO}_4$ . Adsorption of  $\text{ClO}_4$  on the bare surface with trace amounts of water can then be considered a model of specific adsorption, where the ion loses part of its hydration shell in order to contact the electrode. Even though the symmetry of the perchlorate has been reduced to  $C_{3v}$  it is still slightly hydrated, as indicated by the vibrational signatures of  $\text{H}_2\text{O}$  in spectra (a) and (c) of fig. 1 and the  $\text{H}_2\text{O}$  TDS curves (a) and (c) of fig. 2.

The two, widely separated peaks for OH stretching in fig. 1(a) that residual water adsorbed along with perchlorate is hydrogen bonded in such a manner that the two O-H bonds are inequivalent. The lower energy band at  $2990\text{ cm}^{-1}$  represents strong hydrogen bonding, which may occur by an O-H species interacting directly either with one of the oxygens of the perchlorate or with the surface. The higher energy band at  $3555\text{ cm}^{-1}$ , which is below the gas phase O-H stretching frequencies<sup>17,18</sup> of 3657 and  $3756\text{ cm}^{-1}$ , represents a weakly hydrogen bonded O-H species. No distinct  $\text{H}_2\text{O}$  scissoring mode or librational mode was observed, but this may be due to a combination of low water coverage and masking by the strong energy losses due to adsorbed  $\text{ClO}_4$ .

### C. H<sub>2</sub>O/ClO<sub>4</sub>/Ag(110): Model Non-specific Adsorption

After adsorption of H<sub>2</sub>O to saturate the ClO<sub>4</sub>-stabilized thermal desorption state, the Cl-O stretches at 1020 and 1220 cm<sup>-1</sup> in fig. 1(a) are replaced by a single band at 1090 cm<sup>-1</sup> in fig. 1(b). Reduction in the number of observed vibrational modes suggests that the C<sub>3v</sub> symmetry of the tridentate ClO<sub>4</sub> has been increased to a more tetrahedral symmetry similar to that of aqueous perchlorate ion, shown in Table I.<sup>12</sup> Hydration weakens the bonds between the perchlorate and the surface such that all of the Cl-O bonds are nearly equivalent. This suggests that the water lifts the perchlorate off of the surface, producing a non-specifically adsorbed anion.

The process of forming of a non-specifically adsorbed anion is depicted in fig. 4 and can be described by the following reactions listed below along with their approximate energy requirements.



First, adsorbed perchlorate "desorbs" into the gas phase, as shown by eqn. (2). The energy cost of this step is the heat of adsorption of ClO<sub>4</sub>. Because ClO<sub>4</sub> adsorbed on the clean surface decomposes to adsorbed Cl and O instead of desorbing molecularly, the heat of adsorption cannot be determined by thermal analysis. In eqn. (3), an electron is removed from inside the metal to just outside its surface, which is the definition of the work function<sup>19</sup> ( $\Phi_m$ ). The work function of clean Ag(110) is 4.2 eV,<sup>20</sup> but a value 0.1 eV

greater is used in eqn. (3) for the  $\text{H}_2\text{O}/\text{ClO}_4/\text{Ag}(110)$  surface on account of the 0.1 V sample bias potential used for recording the energy loss spectrum. Of course, a more direct measurement of work function is needed to have a more accurate value. The perchlorate species and the electron then combine to form perchlorate ion in the gas phase in eqn. (4), gaining the electron affinity (E.A.) of  $\text{ClO}_4^-$ , which has been calculated to be 6.3 eV.<sup>21</sup> Finally, in eqn. (5), the gas phase ion is hydrated and gains the heat of hydration ( $\Delta H_{\text{hyd}}$ ). The calculated value for  $\Delta H_{\text{hyd}}$  of  $\text{ClO}_4^-$  is -2.3 eV.<sup>22</sup> We may also obtain an estimate of the surface hydration energy from the TDS results of  $\text{ClO}_4^-$ -stabilized  $\text{H}_2\text{O}$ . As previously discussed<sup>6</sup> the ratio of peak desorption temperatures of the hydration water  $T_{p,\text{hyd}}$  (190 K in fig. 2) to ice-like water  $T_{p,\text{ice}}$  (162 K) approximates the ratio of the heat of hydration to the heat of sublimation (0.5 eV),

$$\Delta H_{\text{hyd}} = (T_{p,\text{hyd}}/T_{p,\text{ice}}) \Delta H_{\text{sub}}. \quad (7)$$

When eqn. (7) is applied to the TDS peak for  $\text{H}_2\text{O}/\text{ClO}_4$ , the enthalpy of surface hydration of  $\text{ClO}_4^-$  is estimated to be 0.6 eV per  $\text{H}_2\text{O}$  molecule. For the total hydration, this value must be multiplied by the solvation number. From fig. 2 the solvation number is in the range of 3-4, yielding an estimate of 1.8-2.4 eV for the hydration enthalpy, in reasonable agreement with the calculated value.<sup>22</sup>

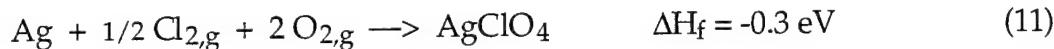
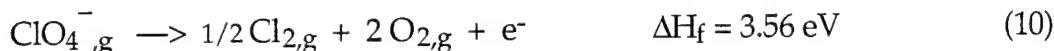
For the formation of perchlorate ion to be thermodynamically favorable, the total free energy of the reaction in eqn. (6) must be less than zero,

$$-\Delta H_{\text{ads}} + \Phi_m - \text{E.A.} + \Delta H_{\text{hyd}} \leq 0. \quad (8)$$

Although some of the calculated values are enthalpies, they can be treated as free energies if the entropic contribution is neglected because of the low temperatures in this work. The minimum value for the heat of adsorption of perchlorate in order for eqn. (6)

to be feasible is found by solving eqn. (8); that value is  $\Delta H_{ads} = -4.3$  eV.

The heat of adsorption can be estimated from the heats of formation of  $\text{ClO}_4^-$  and  $\text{AgClO}_4$  as follows:



The calculated value of -3.0 eV is more positive than the lower limit determined by eqn. (8), suggesting that formation of a fully hydrated perchlorate ion is thermodynamically feasible in UHV.

For coadsorption of  $\text{H}_2\text{O}$  with 0.5 ML of  $\text{ClO}_4$ , the persistence of the Cl-O stretch at  $1240 \text{ cm}^{-1}$  of tridentate  $\text{ClO}_4$  indicates that the ability of water to weaken the bonding of perchlorate to the metal is not unlimited. Even with coadsorption of 0.33 ML  $\text{H}_2\text{O}$ , much of the perchlorate remains adsorbed to the surface. The appearance of a second thermal desorption peak at 210 K in fig. 2(d), corresponding to a solvation energy of 0.65 eV per  $\text{H}_2\text{O}$  molecule using eqn. (7), would suggest stronger hydration of  $\text{ClO}_4$ , making full hydration of  $\text{ClO}_4$  easier. However, the solvation number has decreased from 3-4 water molecules per  $\text{ClO}_4$  to an almost 1:1 ratio, so the total solvation energy per  $\text{ClO}_4$  actually decreases. The decrease in the solvation energy makes it less likely that the perchlorate would be fully solvated.

The decrease in solvation number corresponds to a decrease in the number of sites available for water adsorption. In order for water to lift the perchlorate off the surface, water must first adsorb to the metal, then diffuse along the surface to a perchlorate

molecule. If the surface is covered with  $\text{ClO}_4$ , it is more difficult for enough water molecules to adsorb and diffuse such that the perchlorate can be fully solvated. The absence of a distinct  $\text{H}_2\text{O}$  librational mode suggests that water does not adsorb as it does on the clean surface.

## V. CONCLUSION

Adsorbed  $\text{ClO}_4$  exhibits tridentate coordination on  $\text{Ag}(110)$ . In conjunction with previous LEED and ESDIAD results, the vibrational data have been used to propose a model for this adsorption. Agreement between the EELS spectrum and in-situ IR shows that the adsorbed perchlorate and trace amounts of water can serve as a model for specific adsorption.

When the  $\text{ClO}_4$ -stabilized  $\text{H}_2\text{O}$  adsorption state is saturated for low coverages of  $\text{ClO}_4$ , the vibrational spectrum exhibits modes for  $\text{ClO}_4$  and  $\text{H}_2\text{O}$  similar to those observed in aqueous solution. This suggests a weakening of the bonds between  $\text{ClO}_4$  and the silver surface and non-specific adsorption. However, at the saturation  $\text{ClO}_4$  coverage, perchlorate remains adsorbed to the surface due in part to the lack of free surface for water adsorption. Analysis of the thermodynamics of perchlorate hydration suggests that lifting  $\text{ClO}_4$  at low coverage off the surface by complete hydration is feasible because of the low work function of the  $\text{Ag}(110)$  substrate, the high electron affinity of  $\text{ClO}_4^-$ , and the reasonably high heat of hydration of  $\text{ClO}_4^-$ . At the higher  $\text{ClO}_4$  coverage, the total solvation energy decreases so the complete hydration of  $\text{ClO}_4$  is not as thermodynamically favorable. Similar studies on other metal surfaces are needed to see if this effect extends to other metals, particularly those with a higher work function.

## ACKNOWLEDGMENTS

We gratefully acknowledge the Office of Naval Research for support of this work.

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**Table I**  
 Comparison of internal vibrational modes ( $\text{cm}^{-1}$ ) of adsorbed, complexed,  
 and aqueous  $\text{ClO}_4^-$  as a function of symmetry and geometry.

System	$\text{ClO}_4^-$ , <sup>a</sup>	$\text{M}(\text{ClO}_4)_3$ <sup>b</sup> · $2\text{H}_2\text{O}$	$\text{Cu}(\text{ClO}_4)_2$	$\text{Cu}(\text{ClO}_4)_2$	$\text{ClO}_4^-$ , <sup>a</sup>	$[\text{ClO}_4]^-$	$\text{Ag}(\text{ClO}_4)$ · $\text{H}_2\text{O}$
Symmetry	$\text{C}_{3v}$	$\text{C}_{3v}$	$\text{C}_{3v}$	$\text{C}_{2v}$	$\text{T}_d$	$\text{T}_d$	$\text{T}_d$
Structure	adsorbed alone	tridentate	mono-dentate	bidentate	adsorbed, hydrated	aqueous	ionic
Reference	Fig. 1(a)	[11]	[10]	[10]	Fig. 1(b)	[12]	[11]
$\nu_a(\text{Cl}-\text{O})$	1220	1250-1267	1158	1245-1270	—	—	—
$\nu_a(\text{Cl}-\text{O})$	—	—	—	1130	1090	1110	1030-1160
$\nu_a(\text{Cl}-\text{O})$	1020	1000-1100	1030	1030	—	—	—
$\nu_s(\text{Cl}-\text{O})$	915	970-1000	920	920,948	880 <sup>d</sup>	932	930
$\delta(\text{Cl}-\text{O}),\rho$	640	630 <sup>c</sup>	605,620	600,624	610 <sup>d</sup>	626	620
			648	647,665			

$\nu_a$  = asymmetric stretch,  $\nu_s$  = symmetric stretch,  $\delta$  = deformation,  $\rho$  = rocking.

<sup>b</sup>M=Y, La, Nd, Sm, Gd or Er

<sup>c</sup>average value

<sup>d</sup>shoulder

## FIGURE CAPTIONS

Fig. 1 Electron energy loss spectra of coadsorbed  $\text{ClO}_4$  and  $\text{H}_2\text{O}$  on  $\text{Ag}(110)$ : a) <0.2 ML  $\text{ClO}_4$  + 0.04 ML  $\text{H}_2\text{O}$ ; b) <0.2 ML  $\text{ClO}_4$  + 0.62 ML  $\text{H}_2\text{O}$ ; c) 0.5 ML  $\text{ClO}_4$  + 0.06 ML  $\text{H}_2\text{O}$ ; d) 0.5 ML  $\text{H}_2\text{O}$  + 0.33 ML  $\text{H}_2\text{O}$ .  $\text{ClO}_4$  coverages were determined from LEED patterns and  $\text{H}_2\text{O}$  coverages were determined from subsequent TDS shown in fig. 2.

Fig. 2 Thermal desorption spectra of  $\text{H}_2\text{O}$  coadsorbed with  $\text{ClO}_4$  corresponding to the energy loss spectra in fig. 1.

Fig. 3 Model for tridentate adsorption of a) 0.1 ML  $\text{ClO}_4$  and b) 0.5 ML  $\text{ClO}_4$  on  $\text{Ag}(110)$ .

Fig. 4 Born-Haber thermodynamic cycle for non-specific adsorption of  $\text{ClO}_4$  on  $\text{Ag}(110)$ .

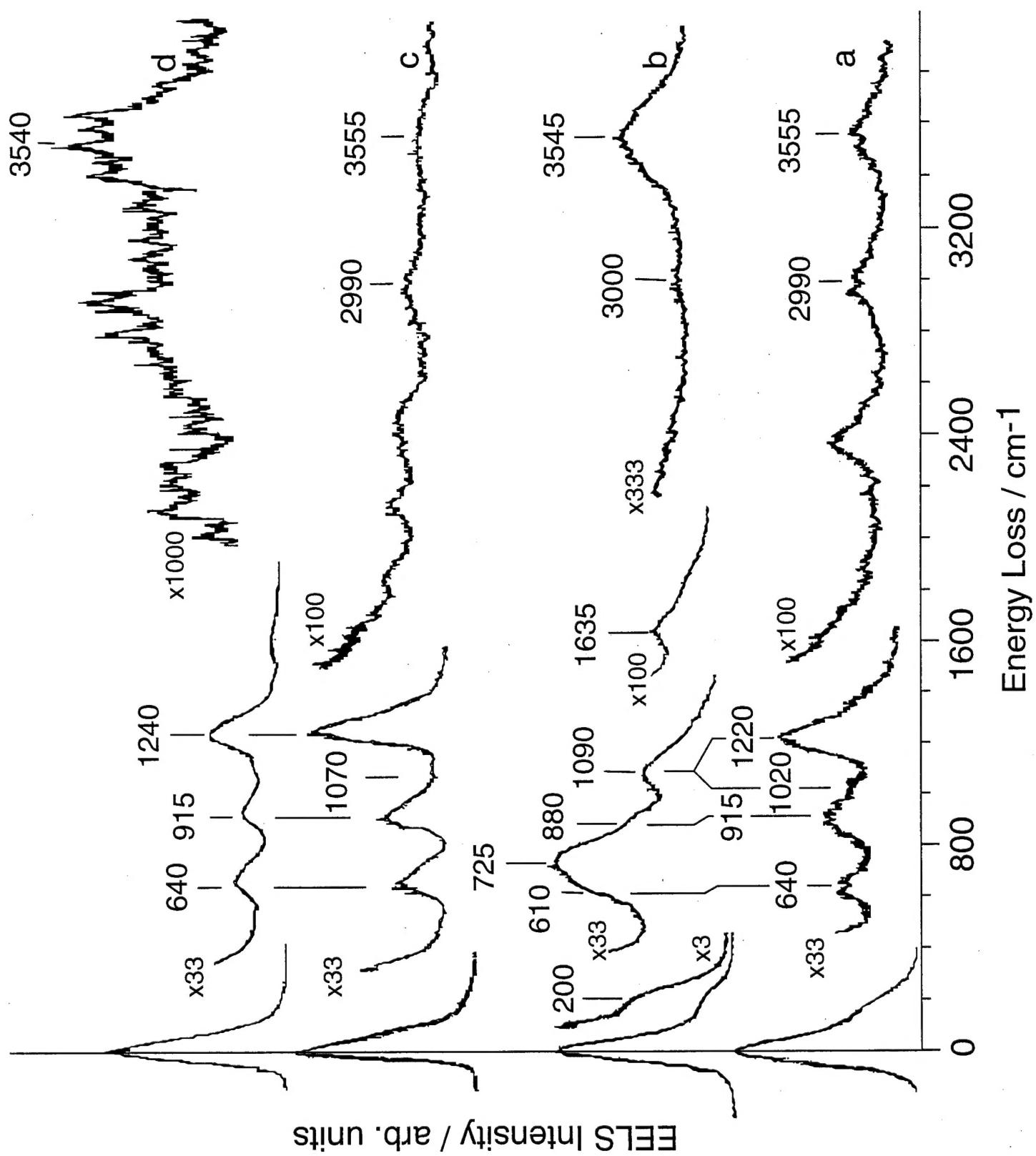


Fig. 1, Krasnopoler and Stuve

## $\text{H}_2\text{O}/\text{ClO}_4/\text{Ag}(110)$

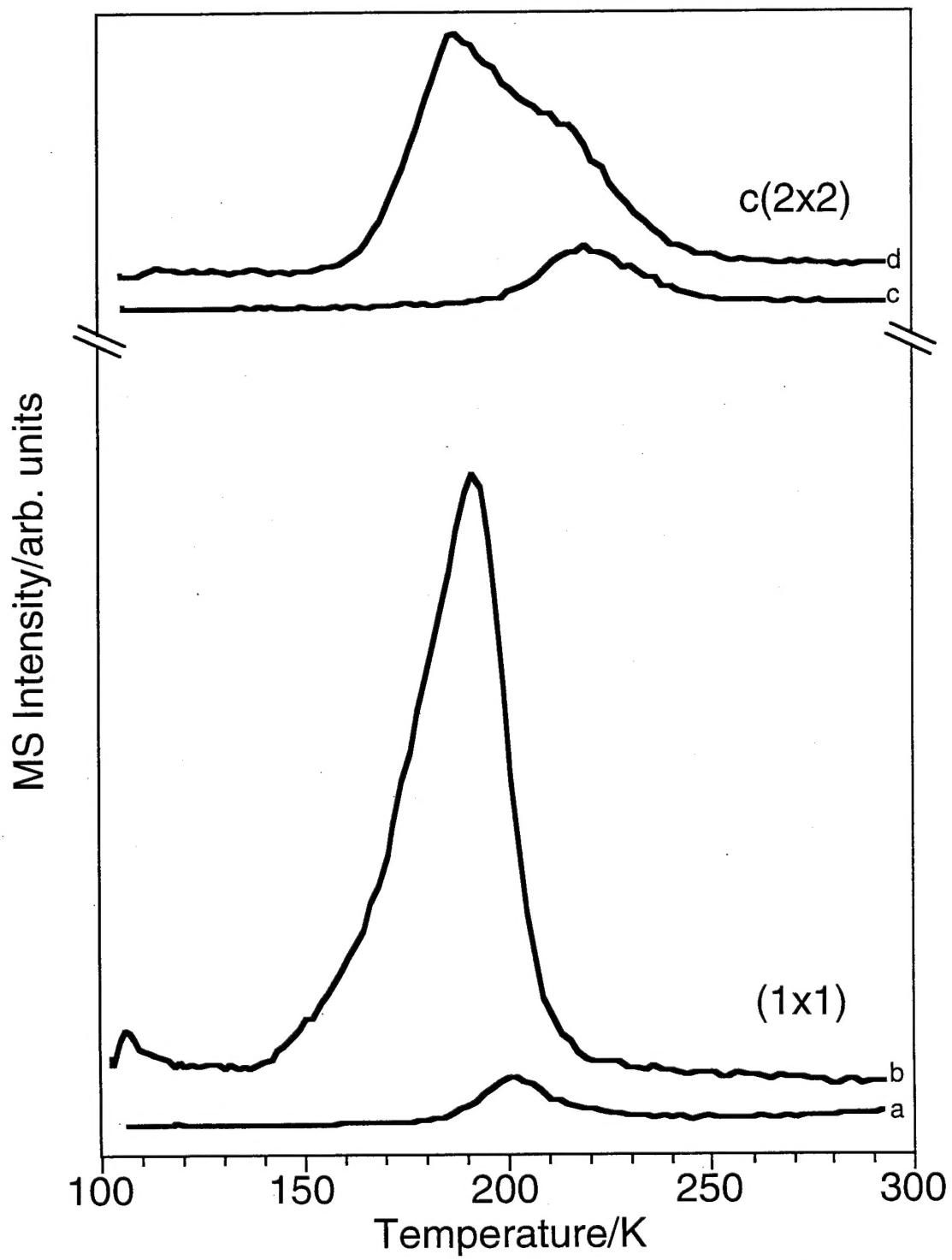


Fig. 2. Krasnopoler and Stuve

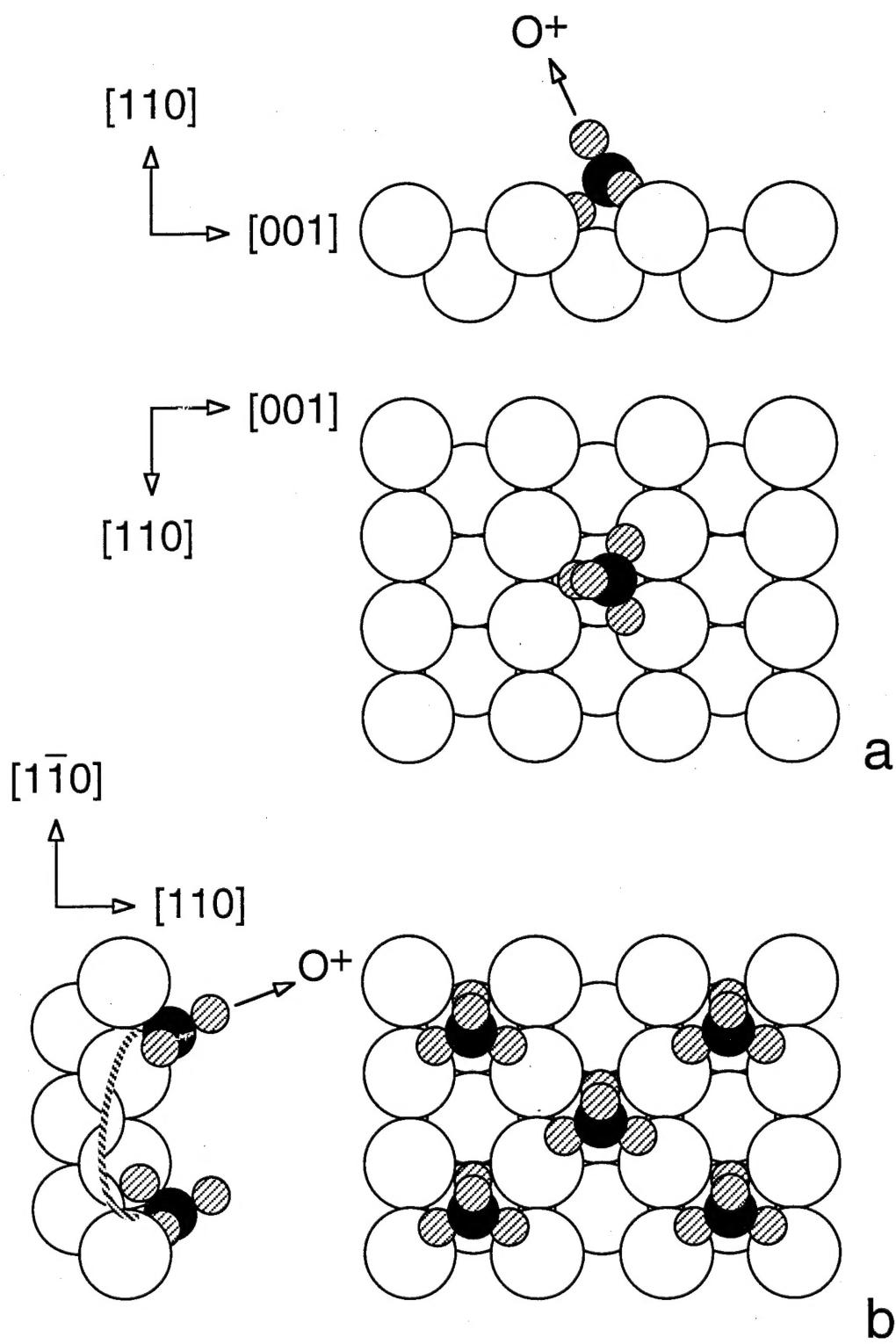


Fig. 3, Krasnopoler and Stuve

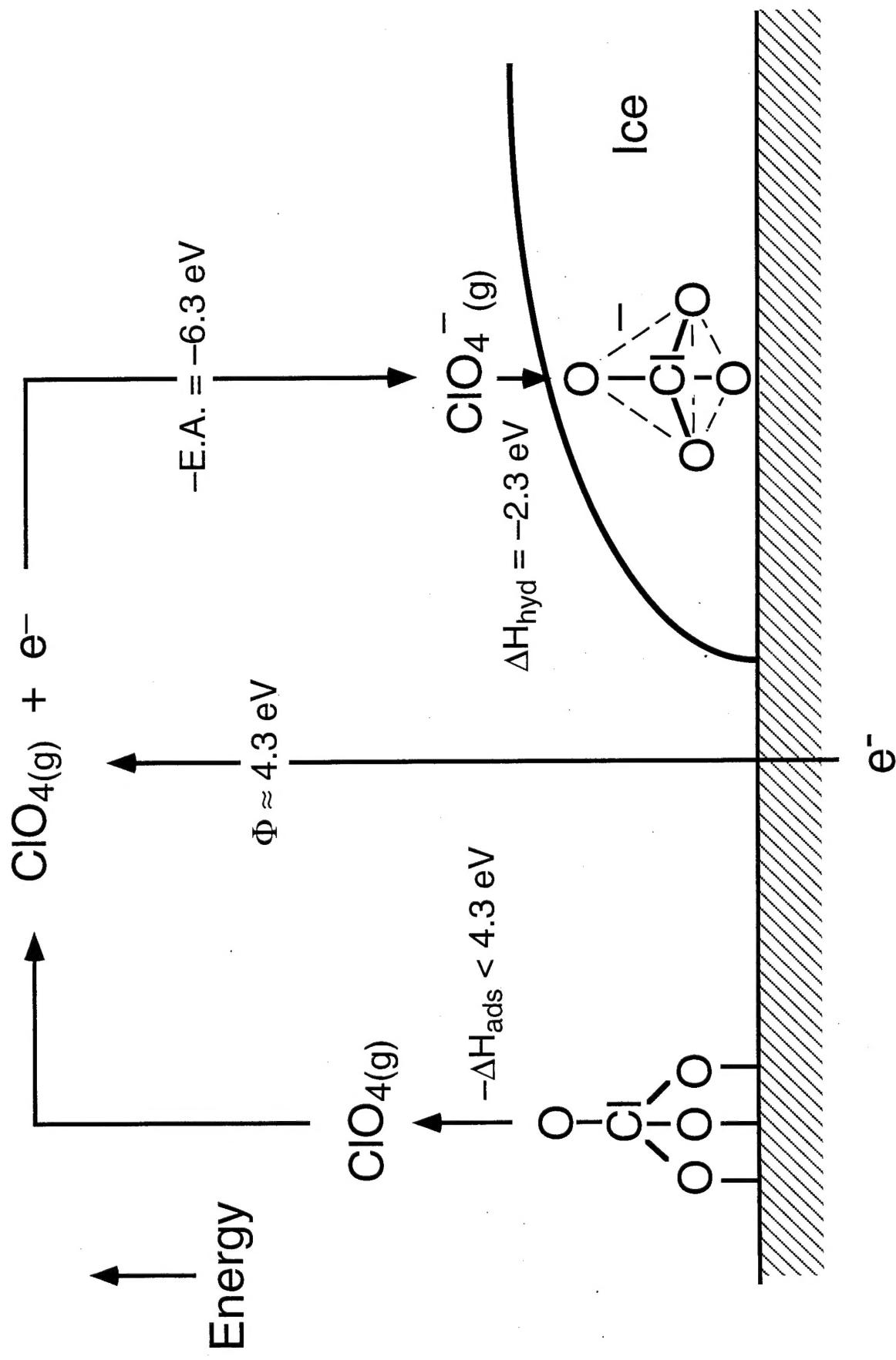


Fig. 4, Krasnopoler and Stuve